

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 0 967 189 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:
29.12.1999 Bulletin 1999/52

(51) Int Cl.⁶: **C04B 38/00**, **C04B 41/53**,
C04B 35/573

(21) Application number: **99304841.2**

(22) Date of filing: **21.06.1999**

(84) Designated Contracting States:
AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE
Designated Extension States:
AL LT LV MK RO SI

(72) Inventors:
• **Aihara, Yasufumi**
Sunnyvale, California 94086 (US)
• **Inoue, Katsuhiro**
Ama-gun, Aichi Pref. (JP)

(30) Priority: **23.06.1998 JP 17594298**

(74) Representative:
Paget, Hugh Charles Edward et al
MEWBURN ELLIS
York House
23 Kingsway
London WC2B 6HP (GB)

(71) Applicant: **NGK INSULATORS, LTD.**
Nagoya-City, Aichi Prefecture 467-8530 (JP)

(54) **A highly resistive recrystallized silicon carbide, an anti-corrosive member, a method for producing the highly resistive recrystallized silicon carbide, and a method for producing the anti-corrosive member**

(57) A highly resistive recrystallized silicon carbide having open pores, wherein layered carbons on the in-

ner wall surfaces of said open pores are removed and a resistivity at room temperature of said recrystallized silicon carbide is not less than 10000 $\Omega \cdot \text{cm}$.

EP 0 967 189 A1

Description

Background of the Invention

5 Field of the Invention:

[0001] This invention relates to a highly resistive recrystallized silicon carbide having a relatively high electric resistance, a method for producing the same, and an anti-corrosive member utilizing the same.

10 Related Art Statement:

[0002] A recrystallized silicon carbide has normally low volume resistivity of about $0.1 \Omega \cdot \text{cm}$ to $50 \Omega \cdot \text{cm}$ at a low temperatures under 500°C , and does not have a characteristic as a semiconductor which features silicon carbide. Thus, a use of the recrystallized silicon carbide has been limited as a refractory.

15 **[0003]** For affording the semiconductive characteristic to the recrystallized silicon carbide, NGK Insulators, Ltd. has disclosed in Japanese Patent application No. 10-72644 that, by controlling a firing atmosphere when recrystallizing silicon carbide, the resistance of the recrystallized silicon carbide can be increased. Although the method was quite effective, it has had still a problem of a fluctuation in the resistance depending on a number of shaped bodies in fire-casing or a shaping position thereof. Moreover, there have been a problem that if a SiC film is formed, by a chemical
20 vapor deposition, on a surface of a substrate, which is composed of a recrystallized silicon carbide having a higher volume resistivity, the resistivity of the substrate is decreased to a value of not more than $50 \Omega \cdot \text{cm}$.

SUMMARY OF THE INVENTION

25 **[0004]** It is an object of the present invention to provide a recrystallized silicon carbide having a large volume resistivity and a method for producing the same.

[0005] It is another object of the present invention to provide an anti-corrosive member on a surface of the substrate by utilizing such a recrystallized silicon carbide, said silicon carbide film having higher anticorrosion and a lower resistivity than that of a substrate.

30 **[0006]** The inventors have investigated the electric resistance in recrystallized silicon carbides in detail. Consequently, they found that the resistivity of the recrystallized silicon carbide is dominated by low resistive layered carbon (C) generated on inner surfaces of open pores and, by removing the low resistive layer through etching, the recrystallized silicon carbide is enabled to have a higher resistance.

[0007] For example, they have successfully produced a recrystallized silicon carbide having a resistivity of not less than $10,000 \Omega \cdot \text{cm}$ by thermally treating it preferably at a temperature of not less than 100°C in a state that it is dipped in a solution of acid, and removing the low resistive layered carbons on the inner surfaces of the open pores so that such carbon is substantially or entirely absent.

35 **[0008]** Any kind of acid can be used if it penetrates into the open pores of the recrystallized silicon carbide and etches the inner wall surfaces of the open pores. It is preferable, however, that a solution of acid contains at least hydrofluoric acid. In this case, it is desirable that the acid solution is a mixed solution of hydrofluoric acid and nitric acid, or a mixed
40 solution of hydrofluoric acid, nitric acid, and sulfuric acid.

[0009] Etching temperature is preferably not less than 100°C , more preferably not less than 150°C .

[0010] The recrystallized silicon carbide preferably has a following characteristic.

- 45 (1) A porous sintered body having an amount of impurities of not more than 0.5 wt% except Si and C and a relative density of 80% to 90%.
(2) A porous sintered body having an amount of impurities of not more than 2.0 wt% except Si and C and a relative density of not less than 70%.

50 **[0011]** The pre-etched recrystallized silicon carbide can be produced by a normal method, in which a shaped body is formed from powdery raw material of silicon carbide by a casting, etc., thereafter, is thermally treated at a temperature of 2200°C to 2400°C , for example, and thereby the recrystallized silicon carbide can be obtained.

[0012] This invention also relates to a higher resistive recrystallized silicon carbide with open pores having a resistivity of not less than $100,000 \Omega \cdot \text{cm}$ at room temperature, in which an amount of impurities except Si and C is not more
55 than 0.2 wt% and layered carbons on the inner surfaces of the open pores are at least partially removed, preferably absent.

[0013] The inventors also have investigated many kind of firing method for attaining still higher resistance, too. Consequently, they found that, by heating a shaped body to a given temperature range of 1600°C through 2000°C from

room temperature under a pressure of not more than 0.01 atm, introducing the inert gas up to a pressure of 0.5 atm to 2 atm, and thereafter heating the resulting material to a temperature in a range of 2200°C to 2400°C, the recrystallized silicon carbide is enabled to be highly purified and by thermally treating the highly purified-recrystallized silicon carbide at a temperature of not less than 100°C in a state of dipping it in a mixed acidic solution, the low resistive layered carbons can be removed, and thereby the recrystallized silicon carbide having a resistivity of not less than 100,000 $\Omega \cdot \text{cm}$ at room temperature can be produced.

[0014] In that case, it is preferable to heat the shaped body to a temperature in a range of 1600°C through 2000°C from a room temperature at a pressure of not more than 0.01 atm, thereafter introduce an inert gas to a pressure of 0.5 atm to 2 atm, evacuate up to a pressure of not more than 0.01 atm, introduce the inert gas up to a pressure in a range of 0.5 atm to 2 atm, and thereafter heat the resulting material to a temperature in a range of 2200°C to 2400°C.

[0015] Furthermore, the inventors have conceived an anti-corrosive member, comprising a substrate made of a highly resistive recrystallized silicon carbide and a film of silicon carbide having a resistivity at room temperature of 20 $\Omega \cdot \text{cm}$ to 500 $\Omega \cdot \text{cm}$, covering that surface of the substrate which is exposed to at least corrosive substance.

[0016] In the case of heating a liquid such as an extrapure water or a sterilized water, for preventing it from being contaminated, it is, sometimes, heated by a heater covered with a Teflon resin. Concretely, it is known that the surface of stick-like metallic heat-generating body is coated with Teflon to obtain a heater which is put into a container with a solution, or that the inner wall surface of a container is coated with Teflon and the container is heated from outside. Recently, in addition to the extrapure water and a sterilized water, a super highly pure corrosive solution containing a mixed acid of hydrofluoric acid, nitric acid, hydrochloric acid, aqua regia, or the like have been required to be heated without any contamination of metallic ions or organic substances.

[0017] The purity of the silicon carbide film is preferably not less than 99.9999%. The thickness of the substrate is preferably not less than 8 mm.

[0018] The silicon carbide film is preferably highly purified and composed of a perfect dense body having a theoretical density, which is unlikely to be corroded with various solutions. In the anti-corrosive member according to this invention, an entire surface of a part of the substrate to be contacted with a solution therein is covered with a high purity and dense silicon carbide film, so that the substrate containing a large amount of impurities is not contacted with the solution. Therefore, contamination of the solution to be heated is very little and almost neglectable. Consequently, the contamination degree of the solution can be decreased to a level under ppt demanded for a extrapure water. Moreover, the corrosion rate of the above silicon carbide film is very slow, so that its characteristics can be kept good for a long time. Since the contacting surface of the film to a corrosive substance is directly heated, a heating efficiency to the corrosive substance is higher.

[0019] Especially, since the silicon carbide film contacting to the corrosive substance is controlled to the resistivity of 20 $\Omega \cdot \text{cm}$ to 500 $\Omega \cdot \text{cm}$, a voltage can be applied the film. Thereby, without special means for power supply, the film has an adequate heat-generating value as a heater. If the resistivity of the silicon carbide film is smaller than 20 $\Omega \cdot \text{cm}$, excessive current may be required to pass the electrode, which makes the size of the power supply larger and requires special parts such as a thyristor. If the resistivity is larger than 500 $\Omega \cdot \text{cm}$, the current to the electrode may be small, so that the film does not work as a heater.

[0020] In the case of induction-heating the corrosive substance, if the resistivity is smaller than 20 $\Omega \cdot \text{cm}$, the substrate sometimes suffers from destruction due to thermal shock generated by rapid heating, and if the resistivity is larger than 500 $\Omega \cdot \text{cm}$, the heat generating value becomes small, so that the corrosive substance can not be heated.

[0021] The anti-corrosive member according to the present invention has advantageously a higher heating efficiency to be capable of heating the corrosive substance uniformly, especially because heat is generated at the plane of the film, of which resistivity is controlled uniformly. A large variations of the resistance-distribution of the silicon carbide film causes a current to be concentrated to a position with a low resistance, and thereby an area of a part to be contacted with a solution or a gas in the heat-generating part of the film is decreased relatively, so that a heat-generating efficiency of the film degrades.

[0022] As the above corrosive substance, the above-mentioned corrosive solution is an example. In semiconductor-manufacturing, for example, dense parts to be exposed to a reactive plasma gas are demanded. Such reactive plasma gas as CF_4 , NF_3 , ClF_3 , HF, HCl, or HBr has an intense corrosion. Accordingly, a part to heat the above intensely corrosive gas in an airtight container has been demanded, and the present anti-corrosive member can be applied to such a part.

BRIEF DESCRIPTION OF THE DRAWINGS

[0023] For a better understanding of this invention, reference is made to the attached drawings, wherein:

Fig. 1 is a schematic view showing an equipment for etching a recrystallized silicon carbide in Experiment A, Fig. 2 is a schematic view to explain a measuring method of volume resistivity, and

Fig. 3 is a schematic view showing an equipment for etching treatment to a recrystallized silicon carbide in Experiment B.

Examples:

[0024] In the following examples, the purity of the starting materials was selected so that the sintered silicon carbide body has an impurity amount (components other than Si and C) of not more than 0.2 wt%.

(Experiment A)

[0025] As a starting material, 45 parts by weight of coarse-powdery silicon carbide with the average particle size of 100 μm and 55 parts by weight of fine-powdery silicon carbide with the average particle size of 2 μm were mixed, and thereafter 20 parts by weight of water and 2 parts by weight of binder were added to the thus obtained mixture, to obtain a slurry. The slurry was poured into a mold with a dimension of 100 mm by 100 mm, a depth of 20 mm made of plaster, and thereby a shaped body was formed in a density of 2.6 g/cc and a porosity of 20%.

[0026] The thus shaped body was heated to 2200°C and held in the same temperature for 2 hours under Ar atmosphere of 1 atm pressure, in a high temperature-atmospheric furnace (carbon furnace), to obtain a sintered body of recrystallized silicon carbide.

[0027] Six cc of hydrofluoric acid, 5 cc of nitric acid, and 4 cc of hydrosulphuric acid were mixed and 15 cc of water was added to the thus obtained mixture to obtain a solution of the mixed acid. A rectangular parallelepiped sample with a dimension of 3 mm \times 4 mm \times 40 mm was cut out of the above sintered body. Then, the sample was dipped into the solution of mixed acid in a container 1 and the container 1 was accommodated into a container 3 as shown in Fig. 1, and thermally treated at 150°C for 16 hours.

[0028] In Fig. 1, the container 1 made of Teflon is accommodated into the holding container 3 made of stainless steel and a lid 2 made of Teflon is fitted into the container 1 of Teflon. A lower board 7 is laid below the container 1 and a hole 8 to release a gas is provided below the lower board 7. An upper board 6 is set on the lid 2. The sample is accommodated into the container 1 of Teflon with the solution of the mixed acid, the lid 2 is fitted, the upper board 6 is set. Then, a lid 4 made of stainless steel is fitted to the container 3, the upper board 6 being pressed down by a tightening bolt, and thereafter the sample is heated.

[0029] The temperature in etching with the solution of mixed acid was changed as shown in Table 1 and the holding time at each temperature of etching was 16 hours. The above sample before etching (Comparative Example 1) and each sample shown in Table 1 were measured with respect to a volume resistivity at room temperature. The thus obtained results are given in Table 1.

[0030] In measuring the volume resistivity, as shown in Fig. 2, a rectangular parallelepiped sample 10 with a dimension of 3 mm \times 4 mm \times 40 mm was cut out of each of the sintered bodies. Then, conducting wires 12 made of platinum were wound around four positions of the sample 10 and connected to an ammeter 14 and a voltmeter 13, and the electric resistivity of each of the above samples was measured by a four probe method. For making sure the conduction between the sample 10 and the conducting wires 12, a platinum paste 11 was applied between the conducting wires and the surface of the sample. A constant current was flow between the two outer conducting wires (current terminals) of the four conducting wires 12, and at this time, the voltage between two inner conducting wires (voltage terminals) was measured. The measurement was carried out in a room kept at 20°C. An electric resistivity was calculated from the following equation.

[0031] Electric resistivity = (the width of the sample \times the thickness of the sample \times the voltage)/(the distance between the voltage terminals \times the current)

Table 1

	Acid etching	Temperature at acid etching (°C)	Volume resistivity at room temperature ($\Omega\text{-cm}$)
Example 1	etched	150	20000
Example 2	etched	100	11000
Example 3	etched	200	22000
Comparative Example 1	not etched	-	5

[0032] As is apparent from the results, the volume resistivity at room temperature of the recrystallized silicon carbide according to the present invention's treatment was remarkably increased. The solution of the mixed acid penetrated

into the open pores of the recrystallized silicon carbide in Example 1 to Example 3 and the inner wall surfaces of the open-pores were etched. The temperature in the above etching is preferably not less than 100°C, more preferably 150°C to 200°C.

5 (Experiment B)

[0033] In a similar way to Experiment A, a shaped body was formed, and thereafter accommodated into a firing furnace having a interior volume of 1000 liters and an effective volume of 200 liters (an interior volume of a casing made of carbon). Then, the furnace was heated up to a temperature of 2300°C in 14 hours under a pressure of 1 atm and held at the same temperature for 5 hours with Ar gas flowing at a rate of 30 liters/min, and thereby a sintered body of a recrystallized silicon carbide was produced. The resistivity at room temperature of the thus obtained sintered body was 2000 Ω·cm.

[0034] Next, the sintered body of recrystallized silicon carbide was set into a CVD equipment, and thereafter a film-forming was carried out at a temperature of 1430°C for 5 hours employing, as gas sources, silicon tetrachloride gas and methane gas. A rectangular parallelepiped sample was cut out, in a dimension of 3 mm × 4 mm × 40 mm, of the recrystallized silicon carbide layer in the thus obtained CVD-SiC/recrystallized silicon carbide-laminate. Then, the resistivity at room temperature of the sample was measured. The thus measured results are given in Table 2 (Comparative Example 2).

[0035] Six cc of hydrofluoric acid, 5 cc of nitric acid, and 4 cc of sulfuric acid were mixed and 15 cc of water was added to the thus obtained mixture to obtain a solution of the mixed acid. As shown in Fig. 3, the layered body 20 composed of the CVD-SiC film 22 and the substrate 21 of recrystallized silicon carbide was dipped into the solution 19 of the mixed acid and accommodated into a container body 15 shown in Fig. 3. Hereupon, the container 15 is made of Teflon, composed of a body 17 and a lid 16, the laminate 20 is accommodated in the container with the solution 19 of the mixed acid. The container 15 was set on a hot plate 18 and heated at a temperature of 150°C for 16 hours. A rectangular parallelepiped sample was cut out, in a dimension of 3 mm × 4 mm × 40 mm, of the substrate of the recrystallized silicon carbide in the laminate after thermally treatment. Then, the resistivity at room temperature of the sample was measured. The thus obtained results are listed in Table 2. Moreover, the volume resistivity at room temperature of the CVD-SiC film after etching was 40 Ω·cm.

Table 2

	Acid etching	Volume resistivity at room temperature (Ω·cm)
Example 4	etched	50000
Comparative Example 2	not etched	30

(Experiment C)

[0036] Followed by a similar way to Experiment A, a shaped body was formed and thereafter accommodated into a carbon furnace. After the interior of the furnace was vacuum-evacuated up to a pressure of not more than 0.01 atm, heating was started. When the interior was heated to a temperature of 2000°C, Ar gas was introduced into the furnace up to a pressure of 1 atm. After the introduction of Ar gas, the interior was heated to a temperature of 2200°C and held at the same temperature for 5 hours, to obtain a sintered body of recrystallized silicon carbide. The resistivity at room temperature of the thus obtained sintered body was 5,300 Ω·cm.

(Comparative Example 3).

[0037] A rectangular parallelepiped sample was cut out, in a dimension of 3 mm × 4 mm × 40 mm, of the sintered body of above Comparative Example 3. Then, the sample was dipped into the same mixed acidic solution as that of Experiment A and thermally treated at a temperature of 150°C for 16 hours. The resistivity at room temperature of the thermally treated sample was 210,000 Ω·cm (Example 5).

(Experiment D)

[0038] In a similar way to Experiment C, the same sintered body of recrystallized silicon carbide as that of Comparative Example 3 was formed. A CVD-SiC film was formed on the sintered body by a similar way to Experiment B, and thereby a laminate composed of the CVD-SiC film and a substrate of the recrystallized silicon carbide was obtained. A rectangular parallelepiped sample was cut out, in a dimension of 3 mm × 4 mm × 40 mm, of the substrate in the

layered body. The resistivity at room temperature of the sample was $50 \Omega \cdot \text{cm}$ (Comparative Example 4).

[0039] The remainder of the laminate after cutting out the sample was etched by a similar way to Experiment B. A rectangular parallelepiped sample was cut out, in a dimension of $3 \text{ mm} \times 4 \text{ mm} \times 40 \text{ mm}$, of the substrate of the recrystallized silicon carbide in the etched layered body.

The resistivity at room temperature of the sample was $170,000 \Omega \cdot \text{cm}$

(Example 6).

(Experiment E)

[0040] In a similar way to Experiment A, a shaped body was formed and thereafter accommodated into a carbon furnace. After the interior of the furnace was vacuum-evacuated up to a pressure of not more than 0.01 atm , heating was started, and, when the interior was heated to a temperature of 2000°C , Ar gas was introduced into the furnace up to a pressure of 1 atm . After the introduction of Ar gas, heating was started again, and the interior was held at a temperature of 2300°C for 5 hours, to obtain a sintered body of recrystallized silicon carbide. The resistivity at room temperature of the thus obtained sintered body was $7,400 \Omega \cdot \text{cm}$ (Comparative Example 6).

[0041] A rectangular parallelepiped sample was cut out, in a dimension of $3 \text{ mm} \times 4 \text{ mm} \times 40 \text{ mm}$, of the sintered body. Then, the sample was dipped into the same solution as that of Experiment A and heated at a temperature of 150°C for 16 hours. The resistivity at room temperature of the thermally treated sample was $10,000,000 \Omega \cdot \text{cm}$ (Example 7).

[0042] As above-mentioned, according to the present invention, a recrystallized silicon carbide with a large volume resistivity and a method for producing the same can be provided. Moreover, an anti-corrosive member having a silicon carbide film, on a surface of a substrate made of highly resistive recrystallized silicon carbide, can be provided with a large anticorrosion and a smaller volume resistivity than that of the surface.

Claims

1. A highly resistive recrystallized silicon carbide having open pores, wherein layered carbons on the inner wall surfaces of said open pores are removed and a resistivity at room temperature of said recrystallized silicon carbide is not less than $10000 \Omega \cdot \text{cm}$.
2. A highly resistive recrystallized silicon carbide having open pores, wherein an amount of impurities except Si and C in said recrystallized silicon carbide is not more than 0.2 wt\% , layered carbons on the inner wall surfaces of said open pores are removed, and a resistivity at room temperature of said recrystallized silicon carbide is not less than $100000 \Omega \cdot \text{cm}$.
3. An anti-corrosive member, comprising a substrate made of a highly resistive recrystallized silicon carbide defined as Claim 1 or 2 and a film of silicon carbide having a resistivity at room temperature of $20 \Omega \cdot \text{cm}$ to $500 \Omega \cdot \text{cm}$, and covering that surface of the substrate which is exposed in use to a corrosive substance.
4. A method for producing a highly resistive recrystallized silicon carbide, comprising the steps of preparing a material composed of a recrystallized silicon carbide having open pores, thermally treating the material in a state of dipping it in a solution of acid and thereby etching the inner wall surfaces of the open pores.
5. A producing method of a highly resistive recrystallized silicon carbide defined as claim 4, wherein the acid contains at least hydrofluoric acid.
6. A producing method of a highly resistive recrystallized silicon carbide defined as claim 5, wherein the acid contains hydrofluoric acid and nitric acid.
7. A producing method of a highly resistive recrystallized silicon carbide defined as claim 6, wherein the acid is a mixed solution of hydrofluoric acid, nitric acid, and sulfuric acid.
8. A producing method of a highly resistive recrystallized silicon carbide defined as any one of claims 4 to 7, wherein the temperature of the thermally treating is not less than 100°C .
9. A producing method of a highly resistive recrystallized silicon carbide defined as any one of claims 4 to 8, wherein

the material is obtained by the steps of forming a shaped body, heating the shaped body to a temperature in a range of 1600°C through 2000°C from a room temperature at a pressure of not more than 0.01 atm, thereafter introducing an inactive gas to a pressure in a range of 0.5 atm to 2 atm and the heating the resulting material to a temperature in a range of 2200°C through 2400°C.

- 5 10. A producing method of a highly resistive recrystallized silicon carbide defined as any one of claims 4 to 8, wherein the material is obtained by the steps of forming a shaped body, heating the shaped body to a temperature in a range of 1600°C through 2000°C from a room temperature at a pressure of not more than 0.01 atm, thereafter introducing an inactive gas to a pressure of 0.5 atm to 2 atm, evacuating up to a pressure of not more than 0.01 atm, introducing the inactive gas up to a pressure in a range of 0.5 atm to 2 atm, and thereafter heating the resulting material to a temperature in a range of 2200°C to 2400°C.
- 15 11. A method for producing an anti-corrosive member as defined in claim 3, comprising the steps of preparing a material made of recrystallized silicon carbide having open pores, thermally treating the material in a state of dipping it in a solution of acid and thereby etching the inner wall surfaces of the open pore, to obtain the substrate.
- 20 12. A producing method of an anti-corrosive member as defined in claim 11, comprising the steps of preparing a material made of recrystallized silicon carbide having open pores, forming a film of silicon carbide with a resistivity at room temperature of $20 \Omega \cdot \text{cm}$ to $500 \Omega \cdot \text{cm}$, by CVD, on at least surface of the material to be exposed to corrosive substance to obtain a laminate, heating the laminate in a state of dipping it in a solution of acid, and thereby etching the inner wall surfaces of the open pores.
- 25 13. A producing method of an anti-corrosive member claimed in claim 12, wherein the material is obtained by the steps of forming a shaped body, heating the shaped body to a temperature in a range of 1600°C through 2000°C from a room temperature at a pressure of not more than 0.01 atm, thereafter introducing an inactive gas to a pressure in a range of 0.5 atm to 2 atm and heating the resulting material to a temperature in a range of 2200°C through 2400°C.
- 30 14. A producing method of an anti-corrosive member defined as claim 12, wherein the material is obtained by the steps of forming a shaped body, heating the shaped body to a temperature in a range of 1600°C through 2000°C from a room temperature at a pressure of not more than 0.01 atm, thereafter introducing an inactive gas to a pressure of 0.5 atm to 2 atm, evacuating up to a pressure of not more than 0.01 atm, introducing the inactive gas up to a pressure in a range of 0.5 atm to 2 atm, and thereafter heating the resulting material to a temperature in a range of 2200°C to 2400°C.
- 35 15. A producing method of an anti-corrosive member defined as any one of claims 11 to 14, wherein the acid contains at least hydrofluoric acid.
- 40 16. A producing method of an anti-corrosive member claimed in claim 15, wherein the acid contains hydrofluoric acid and nitric acid.
- 45 17. A producing method of an anti-corrosive member claimed in claim 16, wherein the acid is a mixed solution of hydrofluoric acid, nitric acid, and sulfuric acid
- 50 18. A producing method of an anti-corrosive member claimed in any one of claims 11 to 17, wherein the temperature of the thermally treating is not less than 100°C.
- 55

FIG. 1

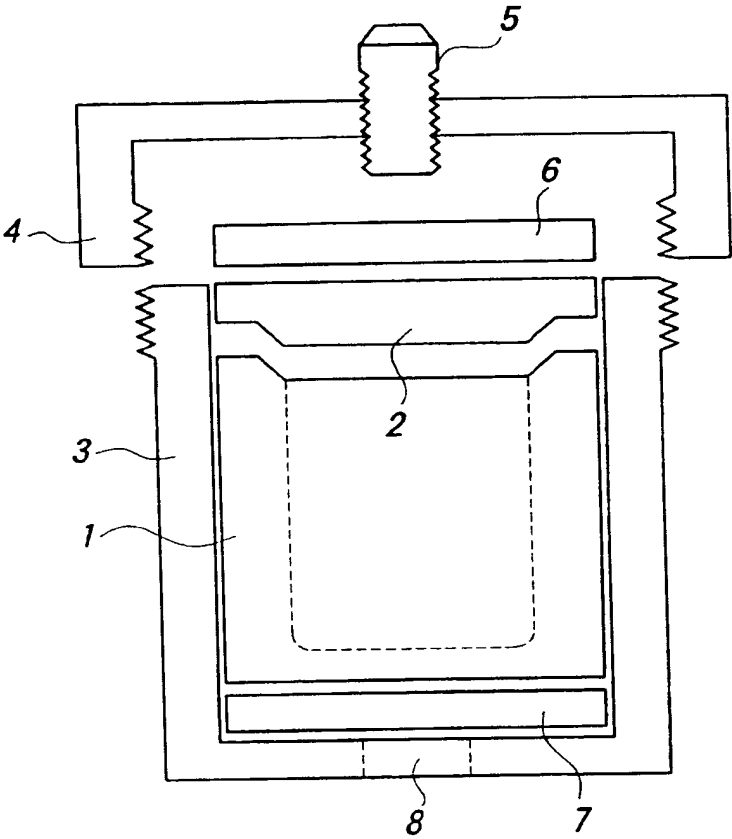


FIG. 2

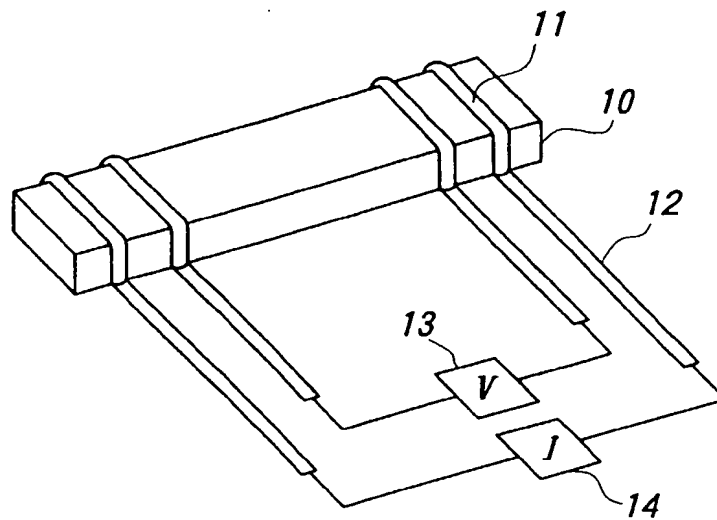
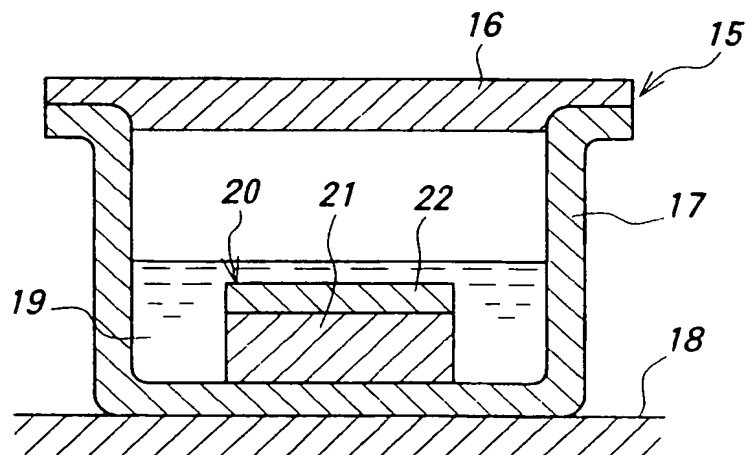


FIG. 3





European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 99 30 4841

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP 0 826 646 A (ASAHI GLASS COMPANY LTD.) 4 March 1998 (1998-03-04) * page 2, line 57 - page 3, line 48; examples 3-5,7 *	1-18	C04B38/00 C04B41/53 C04B35/573
A	PATENT ABSTRACTS OF JAPAN vol. 014, no. 326 (C-0740), 12 July 1990 (1990-07-12) & JP 02 116678 A (IBIDEN CO. LTD.), 1 May 1990 (1990-05-01) * abstract *	1-18	
A	DATABASE WPI Week 7803 Derwent Publications Ltd., London, GB; AN 78-05607A XP002115224 "Silicon carbide body preparation for semiconductors" & JP 52 145419 A (TOSHIBA CERAMICS CO.), 3 December 1977 (1977-12-03) * abstract *	1-3, 12-14	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C04B
The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
THE HAGUE		14 September 1999	Hauck, H
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone ✓ : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

EPO FORM 1503 (03/02) (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 99 30 4841

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

14-09-1999

Patent document cited in search report		Publication date	Patent family member(s)		Publication date
EP 826646	A	04-03-1998	JP 10120466	A	12-05-1998
JP 02116678	A	01-05-1990	NONE		
JP 52145419	A	03-12-1977	JP 1682754	C	31-07-1992
			JP 59010954	B	12-03-1984

EPO FORM P459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

THIS PAGE BLANK (USPTO)

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☐ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☒ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☐ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.

THIS PAGE BLANK (USPTO)